RADIATIONLESS TRANSFER OF ENERGY BETWEEN MOLECULES IN THE TRIPLET STATE

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The self-depolarization of fluorescence and phosphorescence of dyestuff solutions is discussed in terms of FÖRSTER's and JABŁOŃSKI's theories and the criterion for differentiating between triplet-triplet and singlet-singlet energy transfer process is given. In rhodamine B solutions both depolarization phenomena are due to singlet-singlet transfer (in case of phosphorescence via "transition" singlet states of life time of about 10^{-10} sec.) In acridine yellow solutions both transfer processes contribute to the depolarization of phosphorescence.

Introduction

The delayed fluorescence of rigid solutions is partially polarized and the degree of polarization decreases when the concentration of the solution is increased (see e.g. [1] p. 261). In the JABŁOŃKI-scheme (Fig. 1) the process of delayed fluorescence is the following:

$$A + h\nu_e \rightarrow A^* \rightarrow A^{**} \rightarrow A^* \rightarrow A + h\nu_f \qquad (1)$$

where A, A^* and A^{**} denote the ground state, excited singlet state and excited triplet state, respectively, $h\nu_e$ and $h\nu_f$ are exciting and emitted photons. The energy changes accompanied by thermal interactions with the environment are drawn by broken lines in Fig. 1. This picture suggests three kinds of radiationless transfer of energy between an excited molecule A_1^* or A_1^{**} and an unexcited molecule A_2:

$$\begin{aligned} &\text{a)}\ A_1^{**} + A_2 \rightarrow A_1 + A_2^{**} \\ &\text{b)}\ A_1^{*} + A_2 \rightarrow A_1 + A_2^{*} \\ &\text{c)}\ A_1^{*} + A_2 \rightarrow A_1 + A_2^{**} \\ &\quad\ A_1^{**} + A_2 \rightarrow A_1 + A_2^{*} \end{aligned} \qquad (2)$$

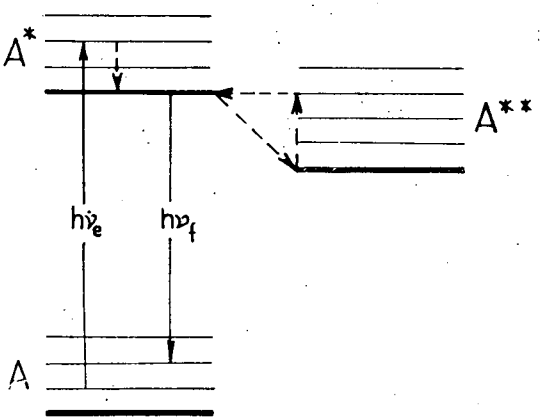

Fig. 1. Jabłoński-scheme

According to some authors (e. g. FEOFILOV [2], ERMOLAEV and SHVESNIKOV [3] energy transfer between states of different multiplicity — as shown under a) and c) ß is impossible, therefore to explain the existence of the self-depolarization of delayed fluorescence only process b) should be considered. According to these authors process b) should be completed during the very short lifetime of the molecule in a transition singlet state. This lifetime, however, is comparable with the lifetime of the excited singlet state. A self-depolarization of the low temperature phosphorescence (process: $A+h\nu_e \rightarrow A^* \rightarrow A^{**} \rightarrow A+h\nu_{ph}$) was observed by SHVESNIKOV and ERMOLAEV [4]. Since the degree of polarization of this process did not change during the decay time, these authors assumed that the depolarization also in this case should be attributed to an energy migration during the lifetime of the transition excited singlet state mentioned above. According to other authors (e.g. LAFFITTE [5], BAUER and coworkers [6], PORTER and WRIGHT [7]) an energy transfer also from the state A^{**} is possible because for the system consisting of molecules A_1^{**} and A_2 the rule of conservation of spin is valid in process a). Process a), in addition to energy transformation, involves also a spin transfer from A_1^{**} to A_2. Processes under c) are excluded from the explanation of self depolarization because they do not obey the rule of spin conservation (in additon the second process under c) is very unlike for energetic reasons).

As a result of the above summary, in the self-depolarization of phosphorescence only processes a) and b) may play a part. The aim of the present paper is to find a criterion to decide which is the actual mechanism of energy migration in a particular case.

Theory. According to FÖRSTER [8] the relative degree of polarization of fluorescence is

$$\frac{P}{P_0} = \frac{6\eta_A/\eta}{5+\eta_A/\eta} \tag{3}$$

where η_A and η denote the yield of fluorescence for the fluorescence of the primarily excited molecules and for the total fluorescence, respectively. ERIKSEN and ORE [17] showed that Eq. (3) is a special case of a more general formula. In viscous solutions, however, Eq. (3) is practically equivalent with the general formula. According to ORE [9]

$$\frac{\eta_A}{\eta} = \frac{1+\tau F_{fl}}{1+2\tau F_{fl}}, \tag{4}$$

where τ is the decay time of fluorescence and F_{fl} is the probability of the energy transfer process (Eq. (3) in [9]). On assuming that the frequency of transfer depends on an inverse 6th power law of the distance R;

$$\tau F_{fl} = \left(\frac{R_{F,fl}}{R}\right)^6 = \left(\frac{\gamma}{\xi}\right)^{6/3} = \frac{\gamma^2}{\xi^2}. \tag{5}$$

Here $\gamma/\xi \equiv c/c_F$; $c = \frac{3}{4}\pi R^3 N'$, $c_F = \frac{3}{4}\pi R_F^3 N'$ the concentration of the solution and the so called critical concentration of the solutions, $N' = 6{,}02 \cdot 10^{20} \cdot R_{F,fl}$ is the critical distance of the molecules for which the frequency of fluorescence and that of radiationless transfer of the exciting energy to an unexcited neighbour are equal.

Substituting (5) into (4), considering all pairs of molecules and assuming a random destribution for the whole system of molecules wo obtain:

$$\frac{\eta_A}{\eta} = \int_0^\infty \frac{\xi^2(\xi^2+\gamma^2)e^{-\xi}d\xi}{(\xi^2+\gamma^2)^2-\gamma^4 e^{-11\xi/16}}. \tag{6}$$

The self-depolarization due to process b) should obey Eqs. (3) and (6).

Eq. (6) was obtained by assuming that the frequency of the energy transfer process is proportional to $1/R^6$ as shown in Eq. (5). The frequency of process a), however, should be proportional to $1/R^8$ according to DEXTER [10]. Therefore, instead of Eq. (5) (if the frequency of transfer process in phosphorescence is F_{ph})

$$\tau F_{ph} = \left(\frac{R_{F,ph}}{R}\right)^8 = \left(\frac{\gamma}{\xi}\right)^{8/3} \tag{6a}$$

should be substituted into Eq. (4). This will lead to a rewritten form of Eq. (6):

$$\frac{\eta_A}{\eta} = \int_0^\infty \frac{\xi^{8/3}(\xi^{8/3}+\gamma^{8/3})e^{-\xi}d\xi}{(\xi^{8/3}+\gamma^{8/3})^2-\gamma^{16/3}e^{-11\xi/16}}. \tag{7}$$

The self depolarization due to process a) should obey Eqs. (3) and (7). In Fig. 2 curves *1* and *2* belong to self depolarization of fluorescence due to processes b) and

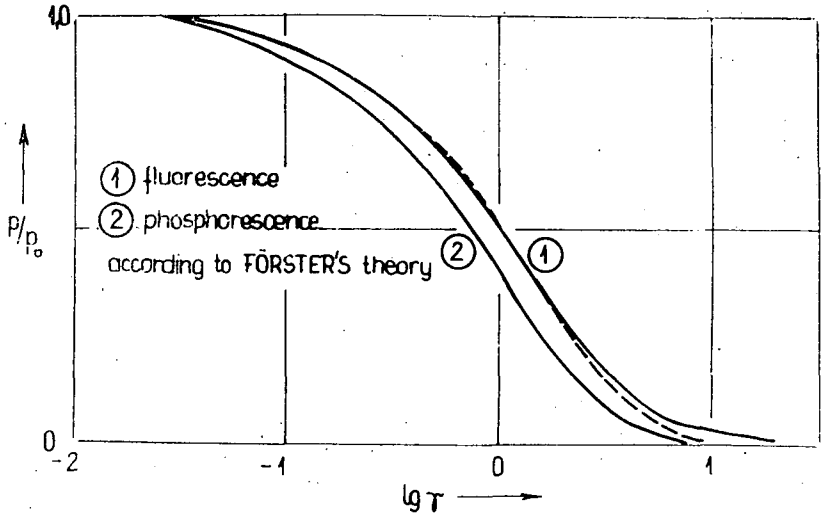

Fig. 2. Self-depolarization of fluorescence according to Eqs. (3) and (6) and self-depolarization of phosphorescence according to Eqs. (3) and (7)

a), they will be referred to as fluorescence and phosphorescence depolarization curves, respectively. Fig. 2 shows that the slopes of these curves are almost the same (for an easier comparison the phosphorescence curve was shifted to the fluorescence curve and is drawn by a broken line).

It is worth to remark that for the comparison of the two depolarization processes JABŁOŃSKI'S theory yields a conpletely similar result. In Fig. 3 curves *1* and *2* are of the same meaning as in Fig. 2. Curve *1* was constructed from the relative emission anisotropy of fluorescence given in [11].

$$\frac{r}{r_0} = \frac{2[v-1+\exp(-v)]}{v^2} \tag{7a}$$

and curve 2 was calculated with

$$\frac{r}{r_0} = \frac{1-v}{v} \tag{8}$$

given in [6] for the relative emission anisotropy of phosphorescence. In these Eqs. $v \equiv 6{,}02 \cdot 10^{20} c_M v$ (c_M is the molar concentration, v is the volume of the effective sphere — a parameter to be determined experimentally). Also in Fig. 3 the slope

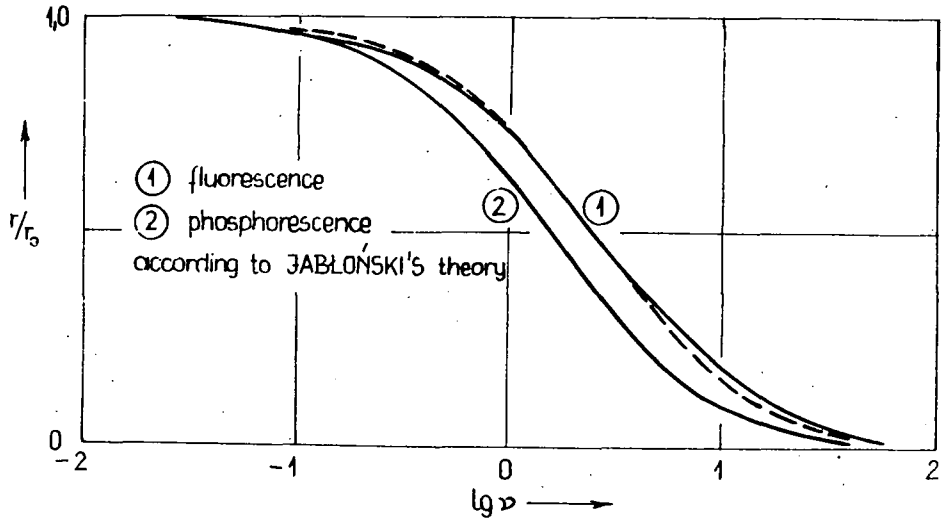

Fig. 3. Self-depolarization of fluorescence according to Jabłoński's theory and phosphorescence in terms of emission anisotropy (Eq. (7a) and (8) respectively)

of phosphorescence depolarization curve *2* (in terms of emission anisotropy $r \equiv 2p/(3-p)$) [12] transferred to curve *1* and drawn by a broken line shows a great similarity to the slope of the fluorescence curve 1. However, the position of the fluorescence and phosphorescence depolarization curves is different, which shows that the critical distances $R_{F,fl}$ and $R_{F,ph}$ or the volumes of the effective sphere are considerably different for the two different processes a) and b). If the radius of the effective sphere is R_i and subscripts *fl* and *ph* denote fluorescence and phosphorescence, the correlations between the parameters for fluorescence and phosphorescence are the following:

$$R^3_{F,fl} = 1{,}32 R^3_{F,ph} \quad \text{and} \quad R^3_{I,fl} = 1{,}58 R_{I,ph}. \tag{9}$$

The differences seem to be high enough to differentiate between process a) and b).

Comparison of theory and experiment. 1. Rhodamine B.

The self-depolarization of the phosphorescence of Rhodamine B in rigid gelatine solution was determined by FRÖHLICH [13], his data are tabulated and were obtained for thin layers (0,03 mm) photoelectrically. The self depolarization of the fluorescence of Rhodamine B in glycerol is known from the paper of FEOFILOV and SHVESNIKOV [14]. Both depolarization data seem to be reliable for a comparison with the theory reported above.

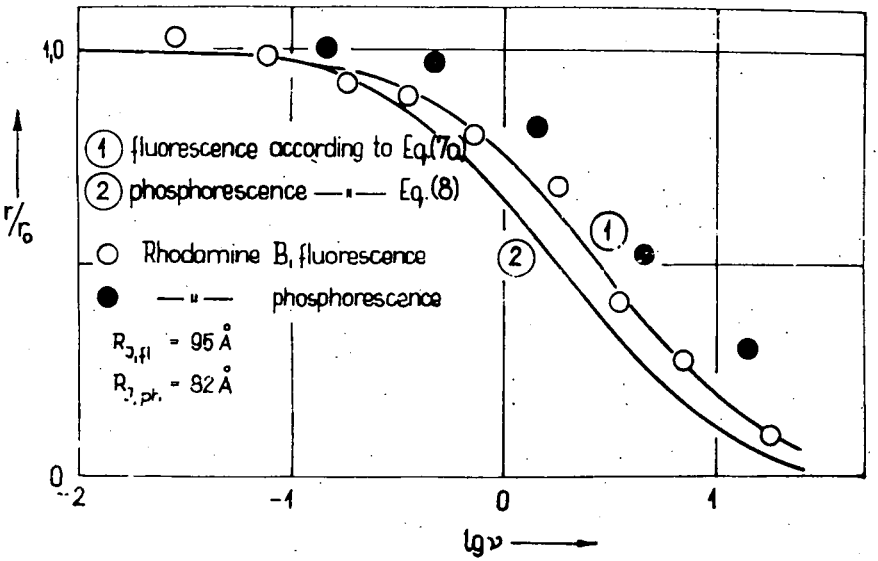

Fig. 4. Comparison of Jabłoński's-theory and experiment

In Fig. 4 the experimental points for the relative emission anisotropies of fluorescence (open circles) practically fall upon the theoretical curve 1 calculated from Eq. (7a) with an effective sphere of volume $v = 3{,}6 \cdot 10^{-18}$ cm^3 corresponding to $R_{I,fl} = 95$ Å in accordance with KAWSKI [15]. (However, ERIKSEN [18] and BOJARSKI [19] obtained 89 Å and 89,5 Å respectively. Irrelevant of which is the correct value the relative shift to $R_{I,ph}$ with Eq. (14) is the same). From Eq. (14) $R_{I,ph} = 82$ Å, and if we plot the experimental values of r/r_0 with an effective sphere of a volume calculated with 82 Å the full circles will be obtained which do not fall upon the theoretical curve *2* for the self-depolarization of phosphorescence from Eq. (8).

In Fig. 5 the same result is shown in relation to Eqs. (3) and (6) yielding the theoretical curve *1* for fluorescence and to Eqs. (3) and (7) resulting in the theoretical curve 2 for phosphorescence. The experimental points of the self depolarization of fluorescence (open circles) fall upon curve *1* with $R_{F,fl} = 72$ Å but the experimental points of the self-depolarization of phosphorescence do not fall upon curve 2.

From the results shown in Figs. 4 and 5 we conclude that both the self depolarization of fluorescence and phosphorescence should be attributed to an energy migration between singlet states according to process b). As a consequence of this

statement we can determine the critical distance for the self-depolarization of phosphorescence empirically by fitting the theoretical curve *1* (fluorescence) to the experimental points (phosphorescence, full circles in Fig. 5). The critical distance for the self-depolarization of phosphorescence obtained in this way is $R_{F,ph}=54$ Å, a much lower value than that for the self depolarization of fluorescence $R_{F,fl}=72$ Å. This

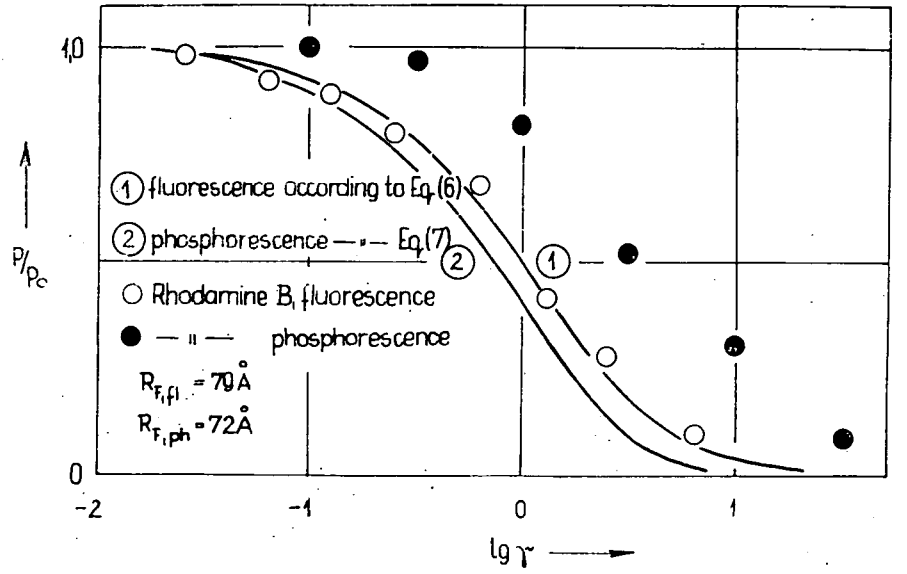

Fig. 5. Comparison of Förster's-theory and experiment

is understandable for the following reasons. The depolarization of phosphorescence should take place as a consequence of the energy migration during the very short lifetime of a transition singlet state. In this short time the equilibrium distribution over the vibrational levels of the interacting molecules cannot be established. However, in deriving Eq. 6 the thermal equilibrium was assumed. Therefore, the critical distance for the transfer should depend on the time elapsing from the instant of excitation until the instant of transfer (or emission). This phenomenon was studied in [16] and was found that in case of Rhodamine B the thermal equilibrium is not established even by the instant of normal flourescence (namely, during the life of the excited singlet state A^*). If the molecules were far from the equilibrium distribution, the critical distance was found to be smaller, in accordance with the present case.

From Eq. (5) the lifetime of the transition excited singlet state, τ_t, can be calculated if we know the life time of the normal excited singlet state, τ. For fluorescence and phosphorescence the equations

$$F_{fl}=\frac{1}{\tau}\left(\frac{R_{F,fl}}{R}\right)^6 \quad \text{and} \quad F_{ph}=\frac{1}{\tau_t}\left(\frac{R_{F,ph}}{R}\right)^6$$

hold, respectively. If we assume that $F_{fl}=F_{ph}$ (considering that the frequency of

energy transfer in both cases belongs to the same process b) and substitute the values $R_{F,fl}=72$ Å, $R_{F,ph}=54$ Å, we have $\tau/\tau_t=R_{F,fl}/R_{F,ph})^6=(79/54)^6\approx 40$, Therefore, the lifetime of the transition singlet state during which the energy transfer leading to the self-depolarization of phosphorescence should take place is $\tau_t=\tau/40$.

2. *Acridin yellow.* BAUER and co-workers [6] obtained in rigid boric acid solution

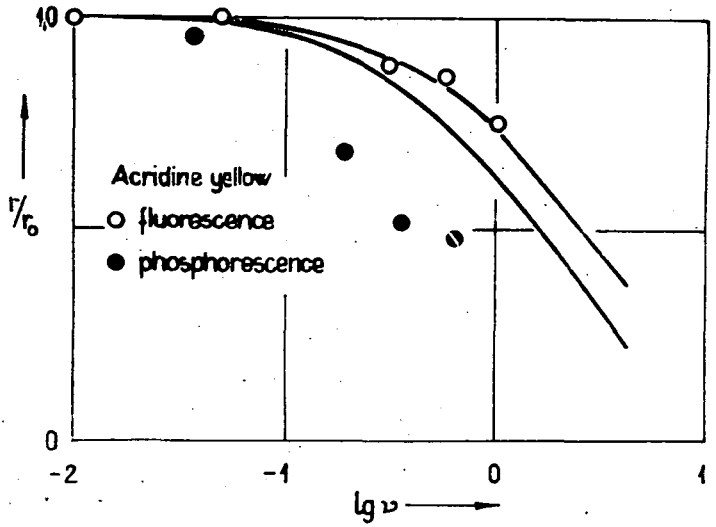

Fig. 6. Comparison of Jabłoński's-theory and experiment

of acridin orange a high self-depolarization of phosphorescence. In Fig. 6 their experimental data are plotted for the relative emission anisotropy of fluorescence (open circles) and phosphorescence (full circles). The upper curve (solid line) calculated from Eq. (7a) fits well to the experimental points with a parameter of $R_{I,fl}=$ $=39$ Å. From Eq. (8) $R_{I,ph}=34$ Å, this parameter, however, does not account for the depolarization of phosphorescence because the experimental points lie below the lower theoretical curve (solid line) from Eq. (8). This means that in this particular case the depolarization of phosphorescence cannot be attributed to process a) only, but also process b) should contribute to the depolarization.

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БЕЗЫЗЛУЧАТЕЛЬНЫЙ ПЕРЕХОД ЭНЕРГИИ МЕЖДУ МОЛЕКУЛАМИ ПО ТРИПЛЕТНЫМ УРОВНЯМ

Л. Салаи

На основе теории Ферстера и Яблонского обсуждается концентрационная деполяризация флуоресценции и фосфоресценции у растворов красителей и даётся критерий различения процессов передачи энергии, происходящихся по триплетным и синглетным уровням. У раствора родамина Б обе деполяризационного явления указывают на наличие передачи энергии по синглетным уровням (в случае фосфоресценции длительность „переходного" синглетного состояния приблизительно 10^{-10} sec). В концентрационной деполяризации фосфоресценции раствора акридина желтого принимает участие обе вида передачи энергии.